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BOSTON UNIVERSITY

GRADUATE SCHOOL

Thesis

WAVE LENGTHS OF CERTAIN LINES IN THE MOLECULAR SPECTRUM OF HYDROGEN

Submitted by

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Historical

The scientific study of spectra started only about 250 years ago when Sir Isaac Newton showed that the refraction of sunlight by a prism was due to the fact that the various colored rays were refracted by different amounts, the red rays the least, and the blue the most. Now this phenomenon had been observed by many others, but they assumed that, in some way, the prism had actually changed the "white" into "colored" light and it remained for Newton to interpret the puzzle. This he accomplished by causing "a pencil of sunlight, which was admitted through a round hole in the shutter of a dark room, to pass through a glass prism and then fall on a screen." [1] This gave what he termed a "spectrum", that is a series of images of the aperture, varying in position and color due to the difference in amount of refraction of the light of different wave lengths.

The refraction of light and the laws governing it were of course well known to Newton having been discovered in 1621 by Snell. Descartes however first published information regarding the constant relation between the angles of refracted light; but neither Snell nor Descartes, apparently, had any idea of the real nature of the phenomenon; whereas Newton was fully aware that white light is a composite of variously colored lights and was able to show that, while refraction varies with rays of different colors, it is constant for a ray of any given color.

This is Newton's great contribution to spectroscopy, but he does not seem to have added much to the laws advanced by Snell. Newton did however insert a lens between the opening and the prism, thus

(1) Spectroscopy by E.C.Baly Vol. 1 P 1 (3rd Ed.)

obtaining better definition. He also adopted a narrow slit instead of a round opening,thus eliminating to a considerable extent the overlapping of the colored images. The narrow slit method of illumination is standard practice today.

The black lines in the solar spectrum were first observed by Wollaston but not explained by him. It remained for Fraunhofer to study their properties and point out their importance. These lines are the now famous "Fraunhofer lines"; and ,in a sense, Fraunhofer is the true founder of our modern science of spectroscopy.

Fraunhofer's work deserves more than passing attention, for while it may well be accepted as a fact that he did not appreciate the actual meaning of these black lines,it is equally true that he recognized their value as known positions from which to make accurate measurements of the angle of refraction of the various colored rays. He succeeded in locating about 700 of these lines and labelled the eight chief lines by letters of the alphabet, "A" being nearest the red and "H" towards the violet end. We now know that the black lines correspond to positions where the images of the slit are less intense, due to the absorption of part of the energy of certain rays by the gases in the outer envelope of the sun.

In addition to this work,Fraunhofer greatly improved the apparatus by placing a convex lens between the slit and the prism,thus focusing the images on a screen. He also used a telescope to examine the spectrum visually. By varying the prisms,he proved that the black lines have fixed positions in the solar spectrum, and that sunlight is deficient in rays corresponding to those black spaces. This work alone would entitle Fraunhofer to a high position;but further than this,he investigated the possibility of measurement of the actual length of light waves. As a result,he developed"the theory of

interference of light so far as to invent and construct for himself the first grating, by means of which he made several measurements of the wave-length of the D line with a wonderful degree of accuracy." [1] The grating method of Fraunhofer is in use today.

Fraunhofer's first grating was made by winding silver wire around a brass frame, keeping the wires evenly spaced. This crude device was the origin ofthe grating used today. Following this, Fraunhofer succeeded in making a grating more closely resembling the modern, by ruling equidistant, parallel, straight lines on a flat glass plate.

The phenomenon of diffraction was observed even prior to Newton's work, for in 1665 Grimaldi noticed that a ray of light was "bent" by the edge of an opaque object, producing not a sharp image but one surrounded by colored bands. He called this effect "diffraction". Grimaldi also observed interference, for he found that light received on a screen from two adjacent sources produced darkness. More thorough work was done on this by Young, who in 1801 published the famous "principle of interference."

Huyghens, in 1678, developed the wave theory of light to explain the known facts. He suggested that light consists of transverse vibrations in the ether; and that particles of the ether, separated by an even number of half wave lengths, would be in the same phase of vibration while those of an uneven number would be in opposite phase and hence neutralize each other, thus explaining interference. In addition, to explain diffraction, he suggested that each vibrating ether particle becomes the source of a vibration system, forming a new wave front. Huygens assumed these secondary waves acted entirely in the direction of propagation of the original wave, but this is not strictly true.

Fresnel investigated diffraction and interference and was able

(1) Baly "Spectroscopy" P 9 Vol.1 (3rd Ed.)

to explain the colored bands of Grimaldi. He showed that all the observations could be explained by means of Huyghen's principle and Young's theory of interference. If homogeneous light is used, we obtain a series of dark and light bands due to interference. If white light is used, colored bands are obtained due to the fact that, with different wave lengths present, the points of maximum or minimam illumination are not identical, and we obtain a row of very closely related, colored, maxima -- a spectrum arranged according to the various wave lengths. The shortest, or violet, appears on the side nearest the central image; and the red, or longest wave length, on the outer side.

So far we have dealt only with the so-called visible spectrum, which is but a small fraction of the whole as this extends in both directions beyond the limits set by the human eye. We have established the existence of ether waves varying in length from 1/10,000 millionth (10^{-10}) millimeter to those of many hundred meters in length. The longer waves fall into the province of wireless telegraphy and are not studied in spectroscopy.

In, 1874, Cornu using photographic methods with the grating published part of the Angstrom Normal Map of the solar spectrum. He finished this in 1880, even including the ultra-violet region. This marks the appearance of spectroscopy as an exact physical science.

Angstrom's map was superseded by the complete normal photographic map of the solar spectrum made by Rowland. In this work, Rowland used his new ruling and mounting of the grating. As he made a new determination of the absolute wave length ofone ofthe "D" lines, his values differ from those of Angstrom. The difference, moreover, varies in different portions ofthe spectrum.(1) Because of Rowland's skill, this scale was universally adopted as the standard of reference.

(1) Transactions of the International Astronomical Union Vol.III-1929

Nature of Spectra

So far we have considered the history of spectra in general, in order that we might trace in greater detail the spectra of atomic hydrogen. In a paper of this nature, there is space for only a rough outline on which to build the more specific statements. Hence the rest of this thesis will be concerned more particularly with the data bearing on atomic hydrogen and recently developed methods.

In Bohr's theory of the hydrogen atom, we have the fundamanetal assumption that the "angular momentum of the normal hydrogen atom multiplied by 2, shall be equal to the elementary quantum of action."[1] This determines the normal radius of the hydrogen atom; and by further development of the mathematical implications, we find that the radii of the orbits (of the electrons) vary as the squares of the quantum numbers, whereas the linear velocities of the electrons vary inversely as the quantum numbers. The transition of an electron from one orbit to another is accompanied by a change in the energy of the atom, that is, if the quantum number is lowered, energy is liberated; but transition to a higher quantum state requires the addition of energy. Bohr made the further fundamental assumption that, when energy was liberated or absorbed in this way, it always occurred in such a manner as to produce or take up a single light quantum. From this, Bohr derived the condition that the frequency, multiplied by the elementary quantum of action, is equal to the difference in the energy values. Mathematically expressed $h\nu = \frac{E}{n} - \frac{E}{s}$, where h is Planck's constant; ν, the frequency; E_n & E_s, the energy values of "n" and "s" orbits respectively. This yields Bohr's spectral formula $\nu = \frac{2\pi^2 z^2 e^4 m}{h^3} \left(\frac{1}{s^2} - \frac{1}{n^2} \right)$. As "s" and "n" run through the whole series of integers, we have a double set of terms. The difference between these terms gives the "line spectra"

(1) Haas "Atomic Theory" Chap. 2 p. 24

of the atom and may occur in either emission or absorption spectra. That is, we can represent spectral lines as differences between spectral terms; and the frequency of every line may be written as the difference between two terms. The fixed term defines the limiting frequency of the series. By means of additive or subtractive combinations, we can derive new spectral lines from those already known. This principle was established by Ritz, in 1908, even before Bohr's theory developed. The intensity of a spectral line depends upon how frequently the transitions occur, since these do not occur with equal ease.

Summerfeld's theory requires for each orbit a "principal quantum number" and a "subordinate quantum number", which can never be larger than the principal. This theory points to a greater number of possible states than does Bohr's. From this, by mathematical deductions, we find that to every principal quantum number there corresponds an equal number of different energy levels. The measurements, made on the fine structure of helium lines, have confirmed this theory. Paschen obtained for $\frac{\Delta \nu_H}{c}$ a value 0.3645 cm - 1 ($\pm$ .0045) as compared with the theoretical value 0.365 cm^{-1}, where $\Delta \nu_H$ is the frequency difference of the hydrogen doublet in the two quantum state of the hydrogen atom.

Balmer (in 1885) discovered the simple numerical relationship existing between the wave-lengths of the individual lines of the Fraunhofer's H_α to H_δ and expressed this in the formula $\lambda = C \frac{n}{n^2-4}$, which has been rewritten as $\nu = R\left(\frac{1}{4} - \frac{1}{n^2}\right)$ and is the so-called Balmer's formula. This formula gives very accurate results in the "optical series" of Hydrogen, of which the first 20 lines have been observed in Plücker tubes together with 13 additional lines in the spectra of

nebulous stars. In the absorption spectrum as many as 50 lines have been noted. This series results from a transition into a 2 quantum end state.

Ritz realized that from his combination principle there must be at least one other series in the infra-red, the first two lines in this predicted series being discovered by Paschen in 1909. This series results from the transition into the 3 quantum end state.

A further series in the emission spectrum, resulting from a transition into the one quantum normal state, was discovered by Lyman in 1914. The first three lines of this have been found in a remote portion of the ultra-violet.

In 1922, Brackett discovered in the infra-red the first two lines of a transition to a 4 quantum end state. He also discovered the 3rd, 4th and 5th lines of the Paschen series.

Pfund discovered in the infra-red region the series known by his name. This series covers the transitions to the 5 quantum end state.

The "R" of Balmer's formula represents a constant frequency (3.291×10^{15} sec^{-1}) as obtained from the observed frequencies of the line and is called Rydberg's constant, because in 1895 he correlated this term with the spectra of other elements and thus revealed it as a factor which is not quite constant, but varies slightly from element to element.

Measurement of Wave-lengths of Light

The actual measurement of the wave-lengths of light was first attempted by Fraunhofer as hadbeen previously recorded; and the improvement made by substituting a ruled glass plate has also been noted. By replacing the glass with speculum metal, we are now able, by using the "dividing-engine", to rule gratings containing as many as 20,000 lines to the inch.

An improvement over the plane grating described above was made by Rowland in 1882. This was a polished speculum metal mirror with a spherical concave surface, so ruled that the lines were evenly spaced upon the chord of the arc instead of the arc itself. If the grating and slit are placed upon the circumference of a circle having a radius equal to one half the radius of curvature of the grating, the spectra are focused around the circumference. This eliminates the need for lenses. With Rowland's largest grating, we can photograph on one plate a range of 320 A approximately normally.

The Echelon diffraction grating of Michelson has high revolving power and is made by putting together a series of perfectly parallel plates of equal thickness, which decrease in size by an equal amount. The slight separation of consecutive orders of spectra reduces the value of this method.

The most important rival of the concave grating is the interferometer as used by Michelson, Fabry & Perot. Michelson's interferometer makes use of the principle of interference by allowing light to be partly transmitted and partly reflected by a silvered mirror so that the two rays after travelling different distances again meet, producing an interference pattern. Fabry and Perot used two plates "half-silvered" on inner sides and set parallel to each other with an air space between. Interference patterns were produced by allowing a beam of monochromatic light to pass through at normal incidence.

Divergence in results, obtained with any of the methods given, has shown the need of standardizing the methods of illumination. Roughly, these may be divided into four classes: flame, ark, spark and luminescence.

The flame spectra, in its simplest form, is obtained by introducing a volatile salt of the desired element into the Bunsen flame.

Due to the limitation of this method to volatile substances, and the short duration of the characteristic flame, various ingenious modifications have been proposed. In spite of these changes, and even with the aid of the oxyacetylene flame, the method is a restricted one, since the rare earth metals and the non-metals cannot be detected in this manner. The band spectra accompanying flame spectra is also a drawback, since, as Bohr has shown, the elementary spectra are of the line type. The main use of the flame is in analytical work.

In the case of the arc, we have a higher temperature than with the flame, and the arc spectrum is correspondingly richer in lines. The advantages of the arc, as a means of obtaining a complex spectrum and as a source for illumination in wave-length measurements, have brought it into general use.

The third method of illumination is by means of the electric spark. The spark occurs between rods of the metal or compound or some conducting substance, as carbon, impregnated with the required material. The spark spectrum will contain, in addition to lines of the element desired, the lines due to oxygen and nitrogen in the atmosphere. By proper modification of the apparatus, it is possible to adapt the spark method to solutions. The use of the electric spark has been applied to the vacuum tube, thus extending the study of the emission spectra into the region of very short wave-lengths. A further distinction of the spark spectra is the "enhancement" of the intensity of lines in certain cases.

The final method, or luminescence, is of course confined to gases, generally under very reduced pressure with a high potential discharge, usually from an induction coil. This method has been adapted to the vaporization of metals, and has given us additional information of considerable importance.

Attempts to measure wave-lengths preceded much of the work we have been discussing; for Fraunhofer, in 1821, published the results which he obtained by the use of his first grating. This grating was the crude affair already described; but the regular spaces, thus formed by the wire winding, gave to the world the idea which has resulted in our present highly refined grating. Fraunhofer used wires of various diameters, thus varying the grating spaces. With this apparatus, Fraunhofer measured the lines B to H inclusive. Considering the roughness of the apparatus and the width of his grating spaces, he obtained excellent results. A further improvement, by ruling equidistant parallel straight lines on a flat glass plate, with grating spaces equal to .0033mm and .016mm, enabled him to get for the D lines values of .0005886mm and .0005890mm, as compared with our present value of about .0005890mm and .0005896mm.

The explanation of the meaning of Fraunhofer's lines by Kitchoff, in 1859, aroused much interest and directed attention to the solar spectrum. While there are certain objections to the use of the solar spectrum as a standard, it is true that the "lines" are very fine and sharply defined, so that very accurate determinations can be made of their positions.(1) As a result, Angstrom measured the wave-lengths of a considerable number of these "lines", and made a map of the solar spectrum placing each line according to its wave length. Angstrom worked with very accurately ruled glass gratings. He included the whole visible spectrum from the "A" line to "H", and in 1868 published this map, called the "Normal Solar Spectrum", with the wave lengths expressed in 10^{-10} meters (to two places of decimals). It is this unit of length that we term the Angstrom unit or Angstrom.

(1) Transactions of the International Astronomical Union. Vol. III - 1929

Angstrom used the standard metre at Upsula as a reference; but, due to an error by Tresca in comparing this with the standard at Paris, the wave-length measurements were a trifle small, the value of the metre being 999.94mm, whereas Tresca gave 999.81mm. Angstrom discovered the error but died before the revision was finished by Thalen. This mapof Angstrom's gave us our first standard of reference and served an useful purpose. Angstrom's corrected map remained the standard until superceded by Rowland's values.

Rowland made use of a reflection grating ruled on a spherical mirror of speculum metal. To secure an accurate ruling, Rowland invented an exceedingly accurate automatic "dividing engine" for ruling his grating. With this he was able to make rulings of 100,000 lines to the inch. The spherical mirror focuses the rays, eliminating the need of a lens for focusing the diffracted rays. The advantages of this method are noticeable; namely, the normality of the spectrum and the relation of the superposed orders. By comparison with the D_1 line (assuming the correct value as 5896.156, a mean of the best measurements) Rowland determined with great accuracy the wave-lengths of the principal lines throughout the spectrum. He then photographed the whole normal spectrum, and from his measurements of the principal lines was able tomap the whole spectrum to the given scale. Unfortunately, Rowland's measurements contain a periodic error which prevents correction of his results by applying a constant factor.

In 1894, Michelson, by use of the interferometer obtained the absolute wave-lengths of the red, green, and blue lines of Cadmium in relation to the standard metre at Paris. The values obtained are considerably lower than Rowland's. Soon after this,

Fabry and Perot, using the interferometer, showed that the difference between these results was not proportional to the wave-length. Kayser proved conclusively that the error was inherent in Rowland's method and exceeds the experimental error of present work.

Adoption of Standards

It will be noted in the above discussion that reference has been shifted from the D lines of sodium to the lines in the cadmium spectrum. The reason for this lies in the greater sharpness of the cadmium radiations. To be adopted as an international primary standard, a line must be able to be measured with the greatest accuracy; which means that the radiations must be as homogeneous as possible. Michelson found the cadmium red line to be the most nearly monochromatic of all those which he examined.

As a result of the work of Michelson, and of Fabry and Perot, the International Union for the co-operation in Solar Research was formed. This association assumed the responsibility of establishing the new standards. A meeting was held at St. Louis in 1904, and another at Oxford in 1905. Two important provisions were adopted:- (1) the wave-length of a suitable spectroscopic line shall be adopted as the primary standard; that the number which defines this wave-length shall be fixed permanently and that all wave-lengths shall be measured in the unit thus defined, and that this unit shall be called the Angstrom. (2) Secondary standards shall be measured by interferometer methods in reference to this primary standard; that secondary standards shall not be more than 50 units apart.

At a meeting in 1907 at Mendon, the Union finally adopted the cadmium red line as the primary standard, with a wave-length of 6438.4696 Angstroms (in dry air at 15^0 C and 760mm mercury pressure.)

This value of the Angstrom is equal to the original Angstrom unit to an accuracy of 1 part in 10,000,000. The difference between the value adopted and that obtained by Michelson is due to slight corrections by Benoit, Fabry and Perot.

At a fourth meeting at Mt. Wilson, in 1910, the values of wave-lengths of lines in the arc spectrum of iron (obtained as specified by the Union) were adopted as secondary standards. It was decided to use tertiary standards, obtained from the secondary by interpolation methods. These measurements were to be obtained by linear interpolation, from photographs taken with concave gratings, of lines adopted as secondary standards. At a later meeting, the use of plane gratings or prism spectographs of high dispersion were also approved for this work. The symbol "I.A." was adopted for the Angstrom to prevent confusion with the original unit of Angstrom and Rowland.

A fifth meeting in Bonn, in 1913, resulted in the adoption of certain secondary standards. For the sake of accuracy, conditions were specified for the use of the iron arc in air for the determination of tertiary standards, as follows:

(a) Arc to be 6 mm in length.
(b) For wave-lengths greater than 4000 A. the current used shall be 6 amp.; for less than 4000 A. to be 4 amps. or less. (if possible).
(c) 220 V direct current to be used, with electrodes 7 mm diam. , the positive pole being above the negative.
(d) An axial portion 2 mm long, taken from the middle ofthe arc, to be used as the light source.
(e) Only lines of the groups a, b, c & d of the Mt.Wilson classification to be used.

The World War interrupted this as well as other scientific work. At a meeting in Rome, in 1922, the work was taken over by the International Astronomical Union. The report of the Standard Wave-length Committee was approved and also a list of secondary and tertiary standards in the spectrum of iron. No wave-lengths lower than 3370 I.A. have yet been approved.

For standard illumination, the Union, at this meeting, adopted the Pfund arc with a current of 5 Amps., or less, at 110 - 250 V. Upper pole to be an iron rod 6 - 7 mm. diam. and an iron oxide bead to form the lower pole. Length of arc to be 12 - 15 mm with radiation taken from horizontal central zone not exceeding 1 to 1.5 mm in length.(1)

In 1925, the International Astronomical Union provisionally adopted specifications for the production of primary standards of wave lengths. In 1927, at Sevres, the International Conference of Weights and Measures adopted the red radiation from cadmium as the fundamental standard for wave lengths.(2) The conditions for the production of the red cadmium line, however, varies in a few details from those proposed by the International Astronomical Union, which has not yet adopted the modification.

At Leyde, in 1928, the Union adopted a list of seven-figure wave-lengths as secondary standards to replace the system of iron standards then in use. The secondary standards of neon, as confirmed in 1925, were retained. It was also recommended that further work be done on the provisional standards.(2)

Photography of Spectrum

The photography of the spectrum offers many difficulties. As we penetrate deeper into the ultra-violet region, it is necessary to replace the usual glass lenses by those made of quartz. In addition, since the gelatin of the emulsion tends to absorb short wave lengths, it is necessary to use a special thin coating of gelatin. In some cases the plates are stained with various dyes to obtain better definition.(3)

As is well known, the ordinary commercial photographic plate is satisfactory only for light within the limits of λ = 2400 to λ = 5000 A. Vogel, however, found that by using certain dyes, the

(1.) Report of International Astron. Union 1922.
(2) Transactions of the Internat'l Astron. Union. Vol.III 1929
(3) Spectroscopy E.C.C.Baly Chap. V, Vol. II 3rd Ed. 1927

sensitiveness of the plate was extended. By experimentation, it was found that the plates became sensitive to the light rays which were absorbed by the particular dye used. Many dyes are used, each having a particular range of sensitivity. It has been found possible to extend the useful range of plates from λ = 2400 to λ = 10,000. With a special emulsion, Abney prepared plates sensitive to rays of λ = 20,000. The time of exposure, however, increases materially with the longer wave-lengths. For general work, probably the best sensitisation of plates can be made by incorporating with the gelatin-silver emulsion a dye such as pinacyanol (a quinaldine derivative). Inasmuch as pinacyanol is not very sensitive to the green, it is improved by adding another dye such as "orthochrome-T". A plate, sensitized in this manner, is known as panchromatic and is quite sensitive to allthe visible spectrum.

It will be noticed that these dyes extend the sensitiveness of the plate in the infra-red and are thus of great value not only to the physicist but also to the astronomer. Some commercial use is also possible, but, unfortunately, many of the dyes are unstable and the plates must be used very soon after preparation. This limits their usefulness.

It is also possible to sensitise ordinary photographic plates by bathing the plate in the proper dye solution. The method requires considerable care and skill; but does not in general yield as satisfactory results as the plates which have the dye incorporated in the gelatin emulsion.

Extension into the ultra-violet region is more difficult as both the glass in lenses and prisms of the instruments and the gelatin emulsion tend to absorb the light of short wave-lengths. To overcome these difficulties, use is made of quartz or fluorite for lenses.

By special treatment, we can obtain a film of silver bromide with only a slight quantity of gelatin present. This gives reasonable results to as far as λ = 1850. No gelatin emulsion, however, can be used in the extreme ultra-violet. By use of a paraffin oil treatment, which causes fluoresence, Lyman has used the vacuum spectograph successfully down to λ = 580 A. This method promises to be a valuable aid to the biological microscopist.

Recent Developments in Wave-length Measurements

The development of the Pfund arc [1] and its acceptance as the standard method of producing the iron standards [2] makes it possible to compare the results of the different observers. Recent work has confirmed the use of the Pfund arc in air.[3]

While considerable work has already been done, the number of lines in the secondary spectrum of hydrogen is so great that there is still much work to be done. The intensities of these lines, also, are so varied that it is tobe expected that many of them will show considerable variation in the values obtained by different observers. From the great number of lines, however, it has been possible to choose a sufficient number of fine lines, suitably spaced in the spectrum, which will give agreement in values sufficiently close so that these values may be adopted as secondary standards.

Among the recent papers on secondary standards should be mentinned that of St. John and Babcock (1921)[4] and by Meggers (1924).[5] More recently Babcock[6] has measured some of the iron and neon lines for secondary standards. The results obtained are somewhat lower than the values adopted by the International Astronomical Union.

(1) Pfund A.H. Astrophys.Journal 27, 297 - 1908
(2) Report of the International Astron. Union 1922
(3) Babcock H.D. Phys. Rev. 31, 918-1928
(4) St. John C.E. and Babcock H.D. Astrophys.Jour. 53,260 -1921
(5) Meggers W.F. Astrophys. Jour. 60, 60-1924
(6) Babcock H.D. Astrophys. Jour. 66,256 -1927

The work leading up to our present investigation is of even more recent date, namely, that of Deodhar,[1] of Gale, Monk and Lee,[2] and of Finkelnburg.[3] Gale, Monk and Lee used a 21 ft. Rowland concave grating with a dispersion of 2.63 A/mm. The work was carefully done. Finkelnburg's work is the latest in publication and covers very completely the lines from λ = 3314 to λ = 4861. It seems probable that Finkelnburg's results are more reliable than those of Gale, Monk and Lee. It should be stated that in comparing results, it is necessary to bear in mind the fact that Finkelnburg made use of the old values of standard lines, while the results obtained here are based on the latest revision of the standards. In addition to this, the synchronous exposure of the hydrogen spectrum and the iron spectrum enabled us to obtain an exact correlation of the two spectra, independent of any shift of the plate, while in the spectograph during long exposures of many hours duration.

Apparatus for Measuring Wave-lengths

In this present research, since the measurements were confined to the range lying between λ= 3500 to λ= 5000, it was found inadvisable to use the dyed plates as the ordinary commercial photographic plates give very good definition from λ = 3500 to λ = 5000.

The apparatus used was that devised by Rowland.[4] This consists of two beams AB and BC mounted on a frame so that the beams intersect at right angles at B. A carriage DE is mounted so that the ends D and E are free to move along the beams AB and BC (See Figure 1, Page 18). However the carriage DE may move, the point B is on the circumference of a circle having DE as a diameter. The slit (in vertical position)

(1) Deodhar D.B. Proc. Roy. Soc.(A) 113,420-1926
(2) Gale, H.G., Monk, G.S. and Lee, K.O. Astrophys Jour. 67,II 89-1928
(3) Finkelnburg,W. Zeitschrift Für Physik 52,27 - 1928
(4) Light Edwin Edser 1907 Ed. P. 461

is placed at B; and a concave grating of speculum metal, with the lines vertical, is mounted at D on the carriage DE. The radius of curvature was about 21 ft. A special form of mounting was used so that the camera was in a vertical instead of the usual horizontal position. The advantage of this method is that it prevents convection currents, which would cause distortion of the image, and increases the accuracy of the resulting photographs. In addition, the Pfund arc was arranged so that only the central portion was used; and the whole apparatus was so arranged as to permit the synchronous exposure of the hydrogen and the iron spectra. (See Figure 2)

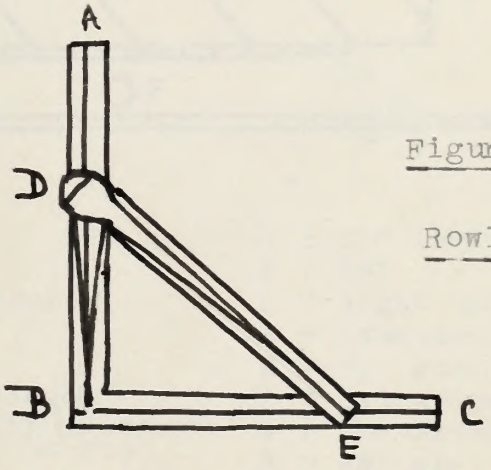
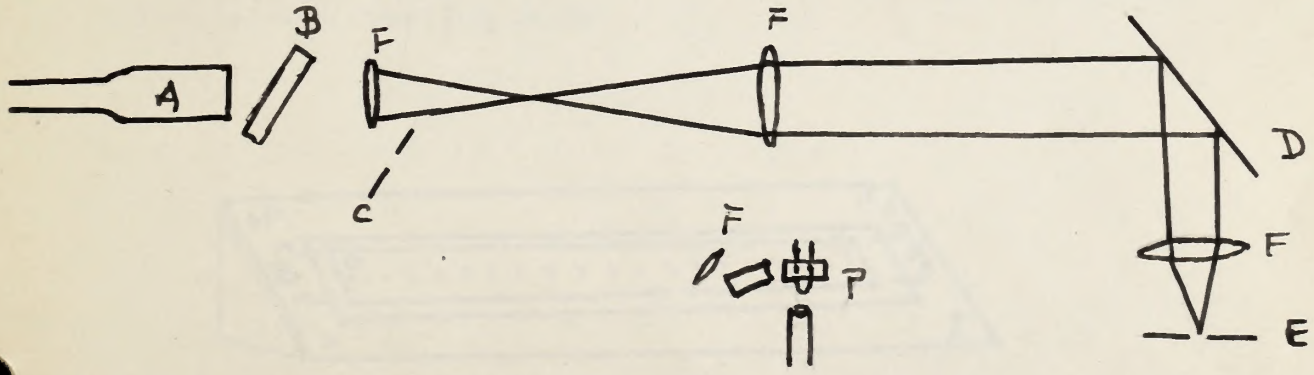


Figure I

Rowland's Mount

Figure 2 Lens System



A = Hydrogen Tube

B = Platinum Mirror (or Quartz Disc)

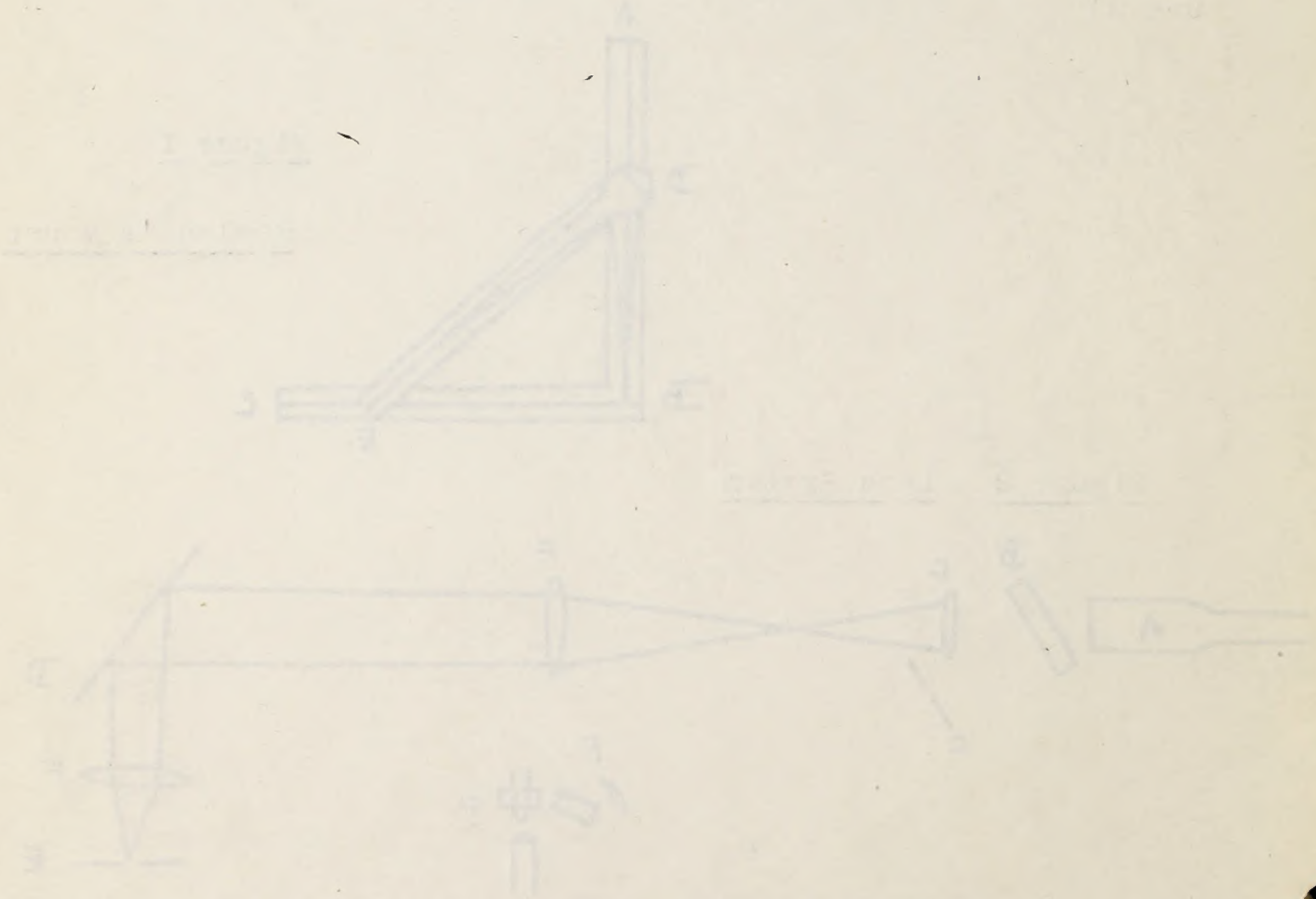
C = Rectangular Opening 1 cm x 2.5 cm.

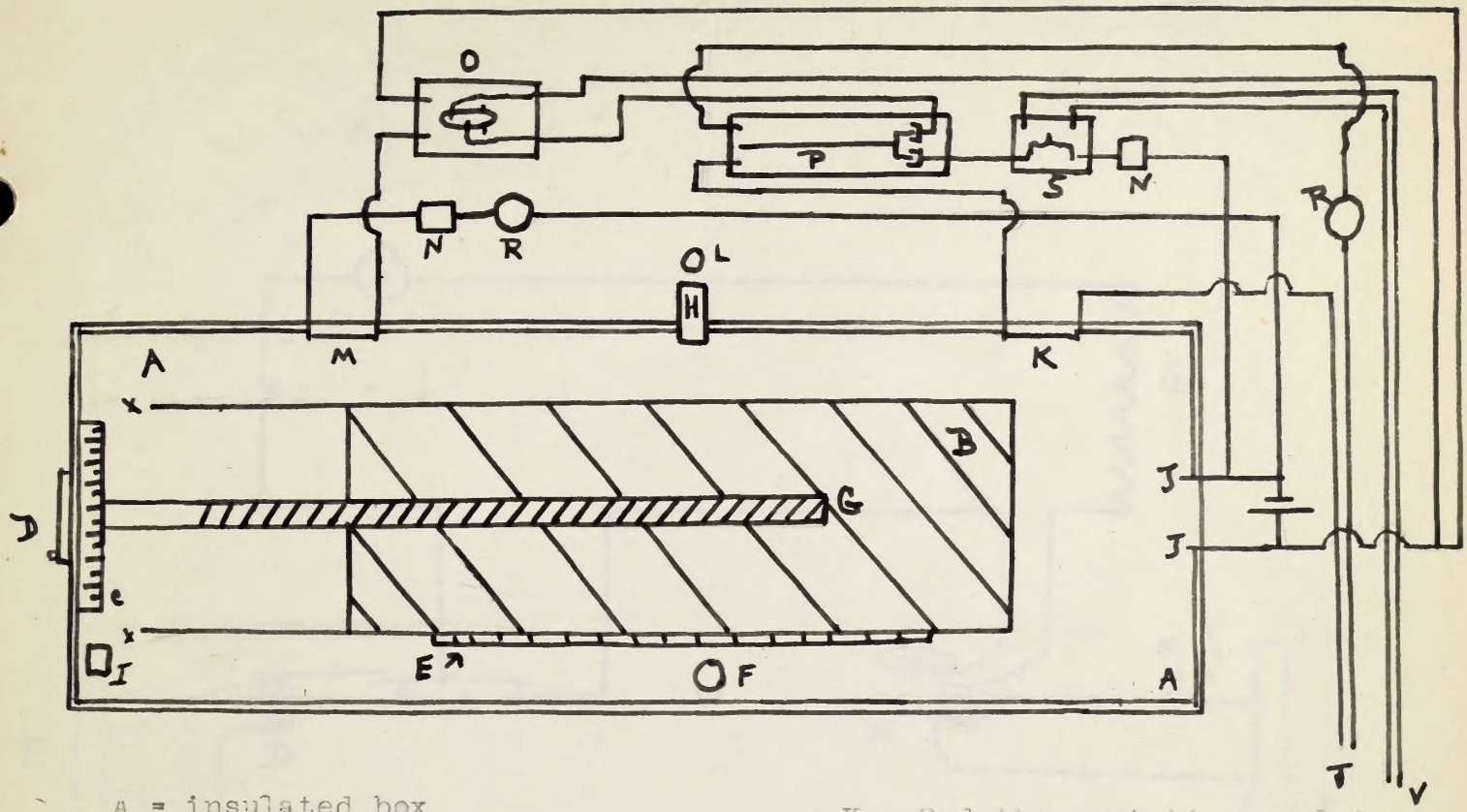
D = Grating

E = Slit

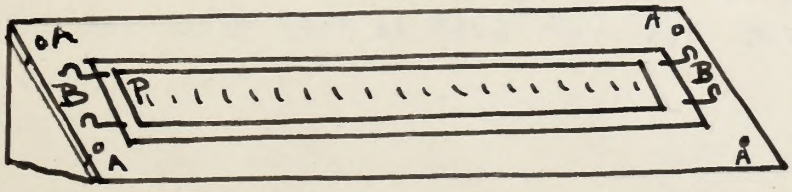
F = Lenses

P = Pfund Arc





A = insulated box
B = carriage
C = graduated dial with vernier
D = hand drive
E = meter bar
x = weights tocontrol carriage
F = telescope eyepiece (with cross-hairs)
G = screw
H = water cell
I = reading window
JJ = nichrome heating unit
K = 2nd thermostatic regulator
M = 1st " "
L = light source
NN = ammeters
O = Hg contact relay
P = telegraph sounder
R = rheostats
S = switch
T = lighting circuit
V = 220 V circuit



Elevation of carriage

A = screw to adjust for parallax
B = clips to hold plate
P = plate

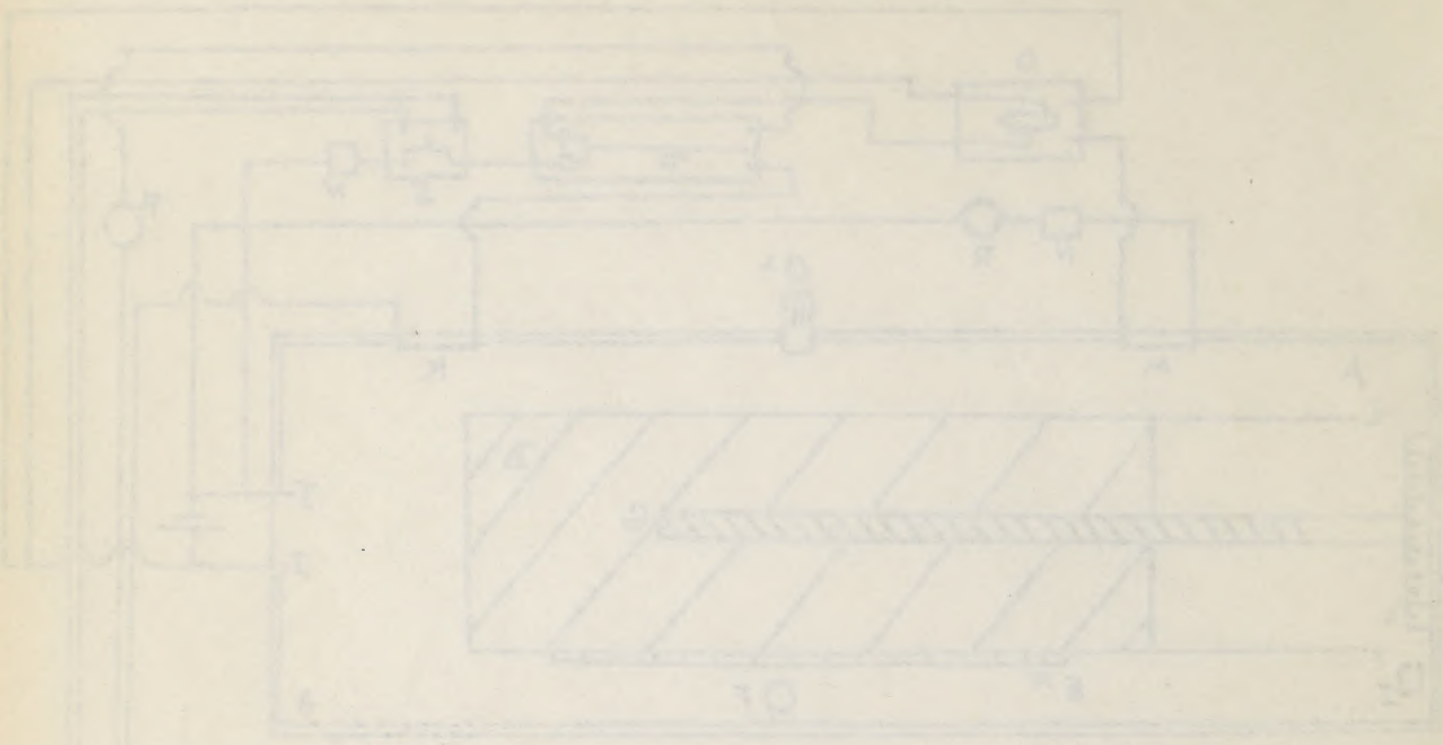
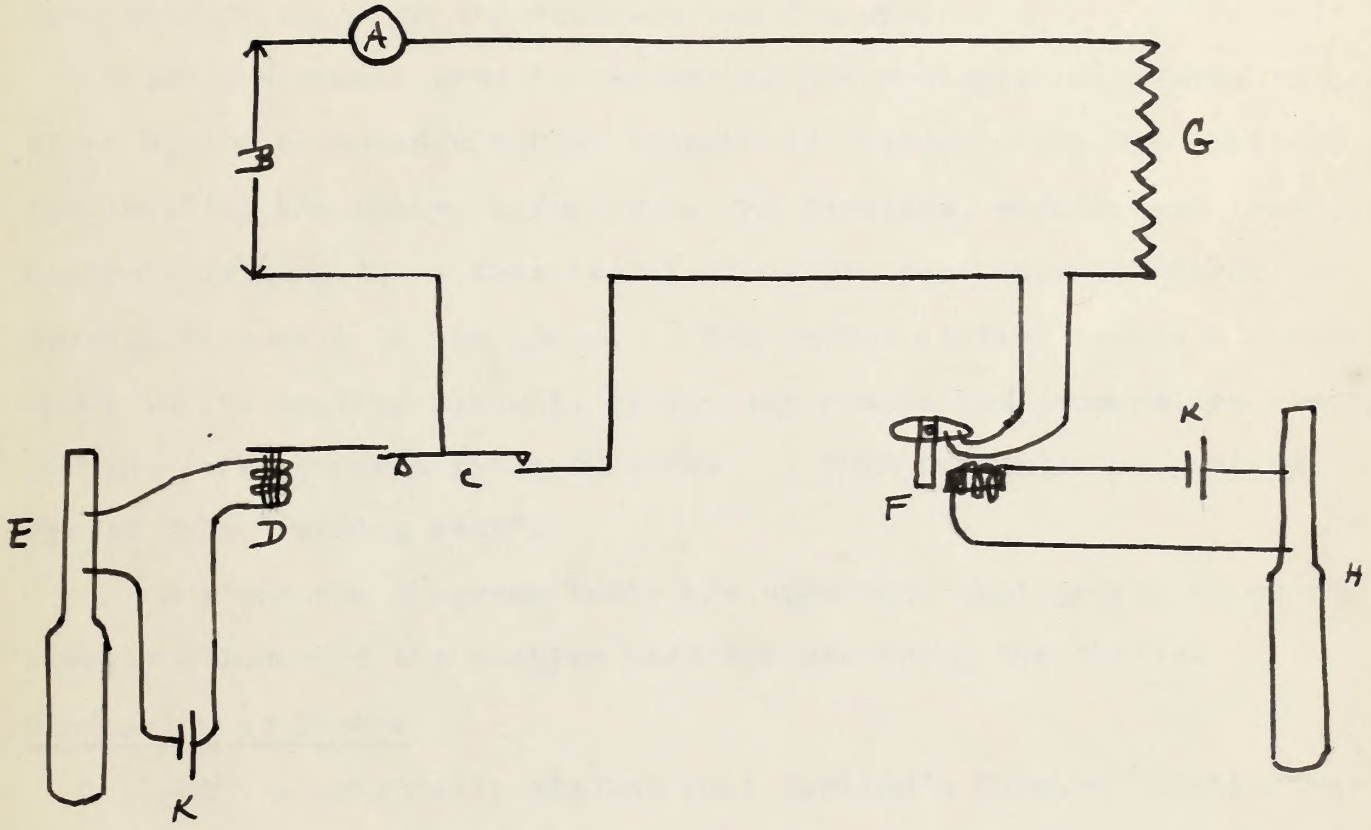


Figure 4

Relay Control for Heating System



A = Ammeter (.9 Amp)

B = 220 Volt line

C = fulcrum (second Mercury regulator)

D = telegraph sounder (second regulator)

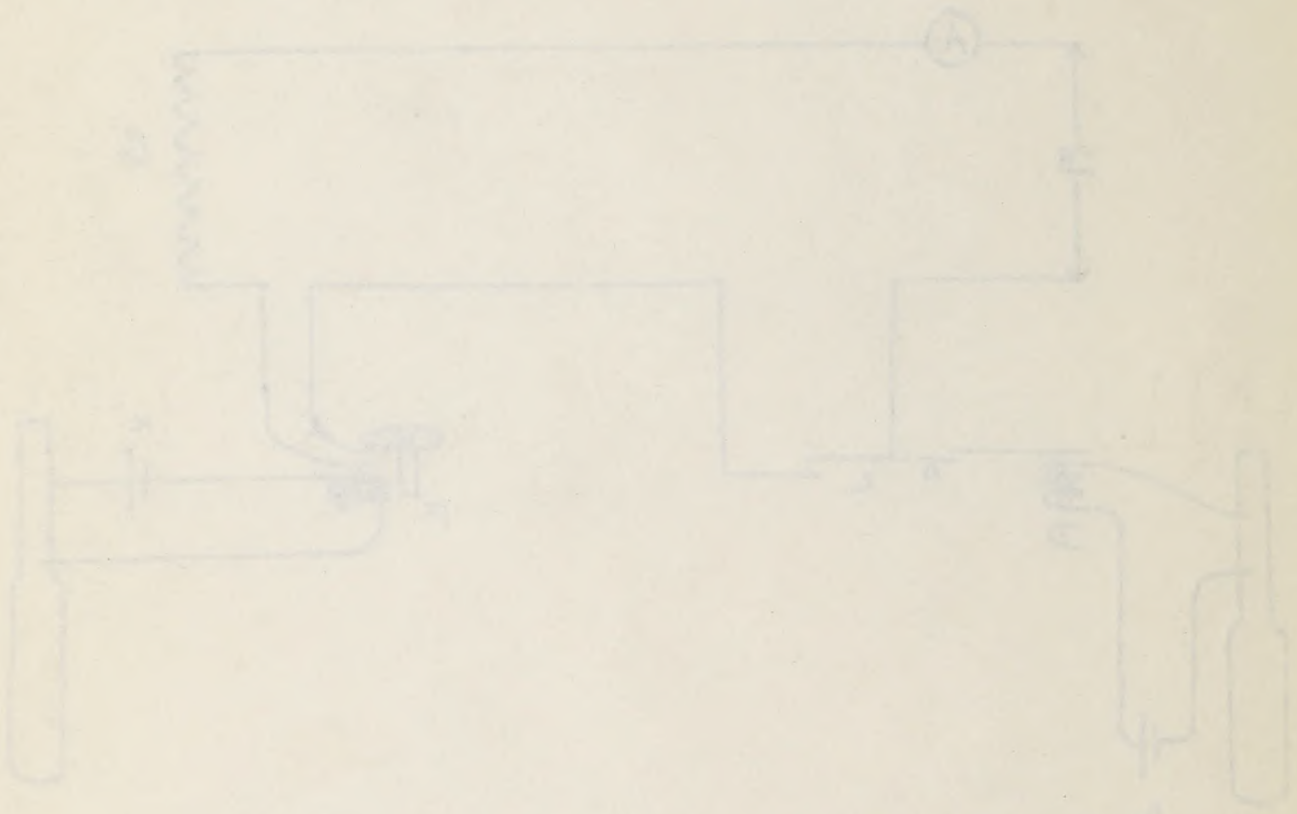
E = Second regulator (Set at 34.1° C.)

F = First mercury contact in circuit breaking relay

G = Resistance of Nichrome wire

H = First regulator (Set at 29.5°C)

K,K Batteries (6 volt)



The hydrogen employed was prepared electrolytically by means of the Hoffman apparatus and dried over phosphorous pentoxide.

In the case of the plate (#14), measured by the writer, the time of exposure, for the hydrogen tube alone, was 12 1/2 hours. With the iron arc, alone, the exposure was 30 minutes in duration. With both tube and arc together the exposure was 7 hours.

The instrument used for measuring the photographic plates is best shown by the attached diagram. (Figure 3) Adjustments are provided for leveling the plate, adjustments for parallax, vernier and temperature control. (Figure 4) This last feature was particularly guarded to prevent expansion of the plate. The second control causes a complete break in the heating circuit, if for any reason the temperature rises, and the first control fails to work. This prevents the heating system from "running away".

Besides the diagrams there are appended photographs to more clearly illustrate the machine used for measuring the plates.

Discussion of Errors

It was originally claimed that Rowland's Concave Grating was superior because it yielded a normal spectrum. We find, however, that the spectra obtained by this apparatus are not sufficiently normal for the degree of accuracy now obtainable. The dispersion is $D = \frac{n}{b \cos \theta}$, where D = dispersion, n = order of the spectrum, b = grating aperture and θ = the angle. In the present instance the radius of curvature equals 21 ft., the length of the plate 41 cm., hence, at about the ends of the plate $\sin \theta = \frac{20.5}{21 \times 30.5} = .032$ radians. Since a radian is very nearly 57.3° we obtain $57.3 \times .032 = 1^{\circ}\ 50'$ (approximately). The cos of $1^{\circ}\ 50'$ = 0.9995. Therefore D, the dispersion, is greater at the ends by about 5 parts in 10,000. Therefore, for a distance equal to half the length of the plate this would give an error of $\pm$ .0013 A in the second order or twice as great (between .002 and .003 A) in the

first order. To avoid this we make use of standards situated short distances apart along the plate. In this way we can consider the spectrum normal between these standards without introducing any appreciable error.

Degree of Accuracy Desired

With the apparatus employed it seems reasonable to expect an agreement within .002 or .003 Angstroms. In the short list given by the writer it will be noted that the average net variation falls well within this limit.

Numerical Results

Measurements made on Plate 14.

TABLE I

λ	NAK	Δ K =F-K	ITC	Δ C = F-C	GML	Δ G =F-G	WF	Aver K&C	Δ KC =F-(K & C)
4171	308	+.001	307	+.002	308	+.001	309	308	+.001
75	161	2	163	0	165	- 2	163	162	1
77	112	1	110	3	(125)	- 12	113	111	2
80	110	- 5	107	- 2	111	- 6	105	109	- 4
82	167	- 1	167	- 1	170	- 4	166	167	- 1
95	671	- 3	666	+ 2	674	- 6	668	668	0
4205	097	+ 5	098	4	098	+ 4	102	097	+ 5
12	495	12	499	8	498	9	(507)	497	-
net variation		+ 12		+ 16		- 16			+ 004
average net var.		+ 1		+ 2		- 2			+0006

In the above table λ stands for the integral part of the wave-lengths, with the fractional portions under the headings of the different observers. The column headed NAK refers to the values

obtained by Dr. N. A. Kent; in a similar way ITC refers to the values obtained by the writer; GML, those of Gale, Monk and Lee; WF, those of Finkelnburg and K and C, to the mean of Dr. Kent's results and those obtained by the writer. The results of Finkelnburg are taken as the standards and the others are compared with them, i.e.: ΔK equals Finkelnburg's, results minus those of Dr. Kent; ΔC is obtained by subtracting the writer's results from Finkelnburg's; in the same way ΔG for Gale, Monk and Lee, and ΔKC for the mean of our work given above. The figures in brackets are considered unreliable. The average net variation (from .001 to .002A) is exceedingly good and if the undoubtedly erroneous figure of 4212.507 obtained by Finkelnburg is discarded, the average net variation of Dr. Kent's values compared with those of Finkelnburg becomes 0, while that of the writer becomes +.0011.

In our laboratory we have found the agreement between the measurements made by the various individuals to be very close. For the best work it is necessary to have one person read the vernier while the other makes the setting.

The following tabulation contains a part of the results of the work in which the writer assisted Dr. Kent in adjusting the position of the various plates upon the comparator, reading the vernier, calculating the wave-lengths and so forth. Comparison is also made with the wave-lengths determined by Gale, Monk and Lee and by Finkelnburg.

TABLE II

λ	Plate 5C	Plate 14	Plate 12	Plate 4A	Mean$_w$	Δ	Finkeln-burg	K-F	Gale, Monk & Lee	K-G
3664			138	145	140	2	(115)	+025	132	+008
65			908	911	909	1	(887)	22	907	2
74			402	402	402	0	(378)	24	398	4
81			975	986	978	3	(951)	27	963	9
84			322	314	318	4	(305)	13	313	5
3796			599	599	599	0	(585)	14	595	4
3944	284			291	289	2	277	12	272	17
62	344			341	343	1	340	3	(328)	15
75	683			678	680	2	689	-009	(666)	14
82	569			576	574	2	562	+012	(537)	37
90	040		042	047	043	1	036	7	031	12
91	843		842	856	846	4	832	14	833	13
97	160			166	164	2	145	19	143	21
4002	507						502		496	
27	391			404	398	6	377	21	377	21
28	342		345	358	349	4	328	21	333	16
43	566			585	579	6	563	16	567	12
62		473		458	468	5	462	6	457	11
65	620			629	624	5	619	5	617	7
66	145			145	145	0	137	8	133	12
69		629		651	636	7	633	3	631	5
	903			904	903	0	893	10	884	19

λ	Plate 5C	Plate 14	Plate 12	Plate 4A	Mean $_w$	Δ	Finkelnburg	K-F	Gale, Monk & Lee	K-G
72	964			971	970	1	958	+ 12	961	+ 11
74	104	096		113	101	5	096	5	100	1
78	847	834			840	7	852	-012	843	-003
87	754	740		762	747	7	745	+002	755	-008
4161	736			736	736	0	745	-009	718	+018
	945			950	947	3	949	- 2	941	6
63	607			604	606	2	608	- 2	605	1
71		308		309	309	1	309	0	308	1
75		161		165	163	2	163	0	165	-002
77		112		116	113	1	113	0	125	- 12
79	597			593	595	2	591	+004	598	- 3
80	108	110		109	110	0	105	5	111	- 1
82		167		173	170	3	166	4	170	0
95		671		674	673	1	668	5	674	- 1
99	788			795	793	2	787	6	793	0
4205		097		107	100	3	102	- 2	098	+ 2
09	177			180	178	2	175	+ 3	169	9
12	498	495		509	498	3	507	- 9	498	0
43	343			353	346	3	348	- 2	326	+ 20
4303	432			435	434	1	437	- 3	423	11
	932			920	928	4	944	- 16	967	- 39
27	933			928	931	2	939	- 8	927	+ 4
32	621			628	624	3	628	- 4	619	5
35	528			529	528	1	532	- 4	519	9
4412	258	255		258	257	1	252	+005	253	+004
18	674			672	673	1	665	8	673	0
19	494			493	494	1	490	4	494	0
20	302			299	301	1	306	- 5	304	- 3

λ	Plate 5C	Plate 14	Plate 12	Plate 4A	Mean$_W$	Δ	Finkelnburg	K-F	Gale, Monk & Lee	K-G
44	224			223	224	0	230	-006	213	+011
49	921			916	918	2	919	- 1	913	5
53	161			171	168	3	160	+ 8	141	27
60		963		967	965	2	971	- 6	965	0
67	143	142		155	145	3	141	+ 4	145	0
86	086			083	085	1	094	- 5	084	+ 1
87	815	817		817	817	0	824	- 7	813	4
93	696			699	698	2	693	+ 5	688	10
98	106			108	107	1	108	- 1	108	- 1
	520	526			524	2	523	+ 1	523	+ 1

As in Table I, the integral parts of the wave-lengths are placed in the column headed "λ". The decimal portions are placed under their proper headings. Plate 5C, 14, 12 , and 4A refer to photographs taken in this laboratory.

Mean$_W$ refers to the "weighted mean" of our plates: valued as follows:

Intensity of line	Weight accorded
2 or higher	1
00, 0, or 1	2
0000 or 000	1

In addition, lines in the first order of spectra were given a weight of 1, while those of the second order were given a double value. The column headed Δ gives the variation of the best line from this weighted mean.

The columns, headed Finkelnburg and Gale, Monk and Lee, give the values obtained by these observers. The column headed "K-F" gives the deviation obtained by subtracting from our values the values obtained by Finkelnburg. In a like manner, we obtain "K-G" using

the values of Gale, Monk and Lee. The figures in brackets are to be considered unreliable.

In Table II, if we include all the figures, we find that our net values are .004 higher than those of Finkelnburg and .006 higher than those of Gale, Monk and Lee. If we discard the bracketed figures, we find our average net variation from Finkelnburg is ± .002; and from Gale, Monk and Lee ±.005. The agreement with Finkelnburg's values is reasonably good. The results of Gale, Monk and Lee seem to be a little low. As previously stated, there is still much work to be done but the meterial included in this thesis gives a fair idea of the present status of our problem.

The attached bibliography gives the texts consulted for the historical data and most of the recent publications on investigations along the lines of this paper. The papers quoted have been read in full, by the writer.

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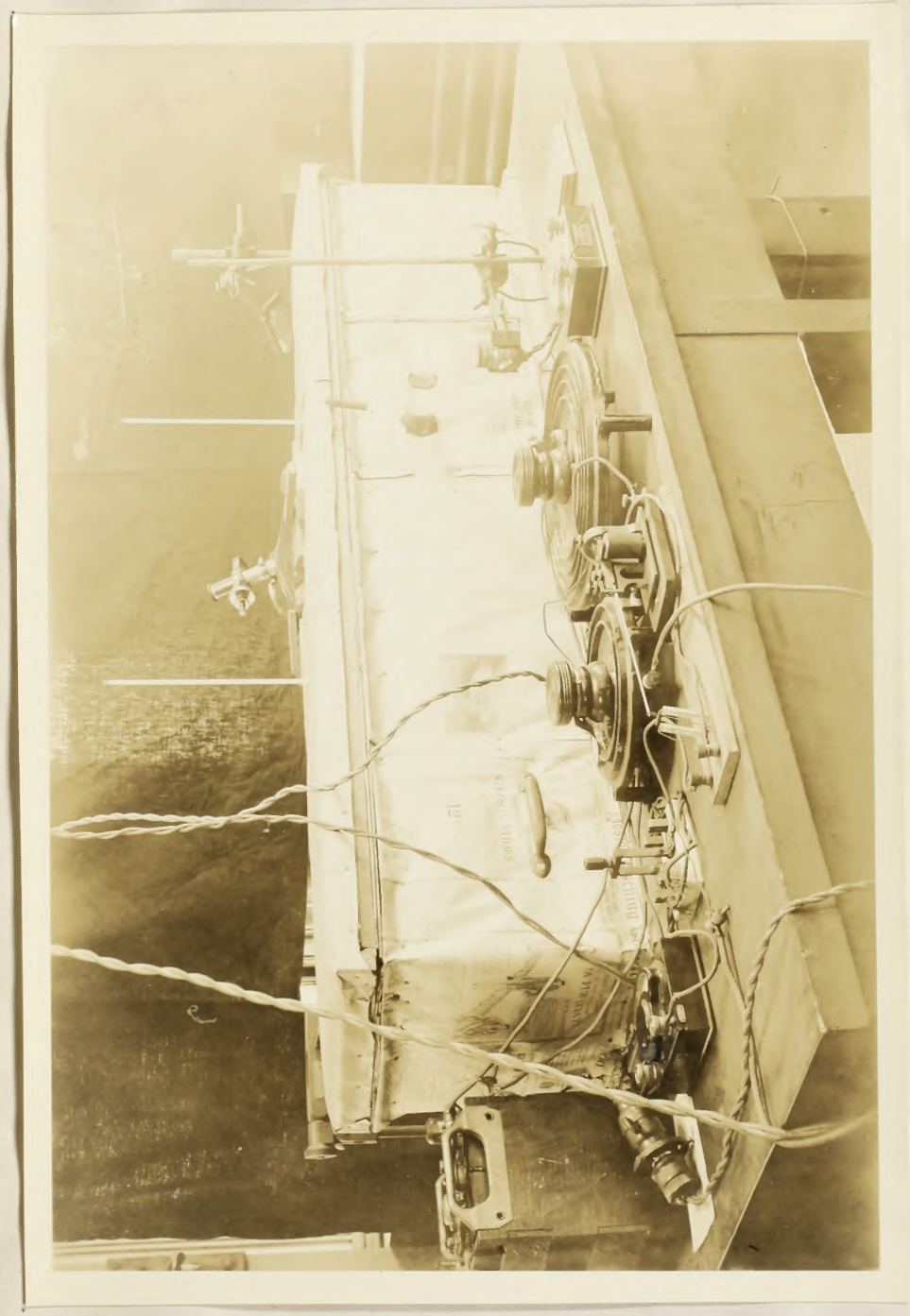

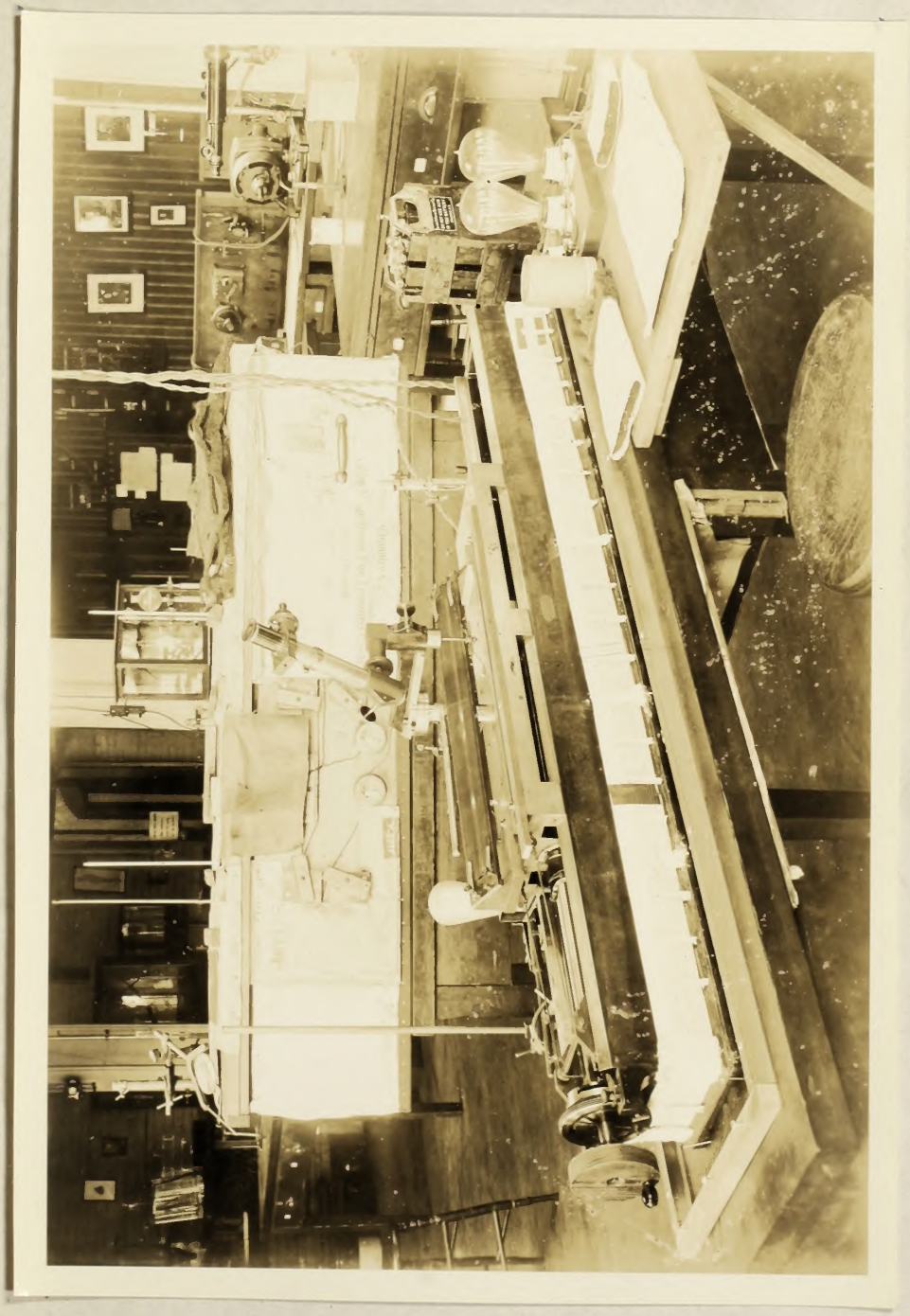

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